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APPLICATION FOR LETTERS PATENT

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**Vapor Forming Devices, and Methods of Cleaning
Vaporization Surfaces**

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INVENTOR

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1 ^{SUB A₁} Vapor Forming Devices, and Methods of Cleaning
2 Vaporization Surfaces

3 ^{INS A₂} TECHNICAL FIELD

4 The invention pertains to methods of vaporizing materials, and to
5 methods of cleaning vaporization surfaces. In further aspects, the
6 invention encompasses vapor forming devices comprising plasma
7 generation circuitry configured to utilize a vaporization surface as a
8 plasma electrode.

9
10 BACKGROUND OF THE INVENTION

11 Vapor forming apparatuses have many applications in modern
12 semiconductor processing. Among the applications is utilization in
13 chemical vapor deposition apparatuses. An exemplary chemical vapor
14 deposition apparatus 10 is described with reference to Fig. 1.
15 Apparatus 10 comprises a reaction chamber 12 having a substrate
16 holder 14 contained therein. A substrate 16 is shown supported by
17 substrate holder 14. Substrate 16 can comprise, for example, a
18 semiconductive material wafer, such as, for example, a wafer of
19 monocrystalline silicon.

20 Chamber 12 has a vapor inlet 18 extending therethrough and a
21 vapor outlet 19 also extending therethrough. Accordingly, a vapor
22 (illustrated by arrows 20) can be flowed through chamber 12.
23

1 Chamber 12 can comprise one or more temperature control
2 mechanisms (not shown) which can include, for example, heaters, or
3 cooling gas flow ports. The thermal controls can enable substrate 16 to
4 be maintained in a temperature such that a material is deposited onto
5 substrate 16 from the vapor 20 within chamber 12.

6 A vapor forming device 30 is provided to generate vapor 20.
7 Device 30 comprises an inlet region 32 configured to enable flow of a
8 non-vapor state material 33 into device 30. Device 30 further comprises
9 an inlet port 34 configured to enable flow of a carrier gas 35 into
10 device 30. Additionally, device 30 comprises an outlet port 36
11 configured to enable vapor-state-material 20 to be output from device 30
12 and into reaction chamber 12 of apparatus 10.

13 A vaporizer 40 is within device 30 and supported by a holder 42.
14 Vaporizer 40 comprises a surface 44 which can be referred to as a
15 vaporization surface. Vaporizer 40 can comprise a heated material such
16 that non-vapor-state-material 33 is converted from a non-vapor-state to
17 a vapor-state upon contacting vaporization surface 44.

18 Material 33 is typically initially in the form of a liquid, and is
19 flowed into device 30 from a holding reservoir 46. Although in the
20 shown exemplary embodiment only one non-vapor-state material 33 is
21 flowed into device 30, it is to be understood that a plurality of different
22 non-vapor-state materials can be flowed simultaneously into device 30 to
23 form a vapor 20 comprising a composite of vapors from the various

1 materials. An exemplary application in which a plurality of non-vapor-
2 state materials are flowed into device 30 is a chemical vapor deposition
3 process for formation of barium strontium titanate (BST).

4 Two separate configurations of prior art vaporizer devices 30 are
5 described with reference to Figs. 2 and 3.

6 Referring first to Fig. 2, a first prior art vaporization device 30
7 is illustrated in diagrammatic, schematic view. Such device comprises a
8 COVA device (COVA Technologies, Inc., 2260 Executive Circle, Colorado
9 Springs, CO 80906).

10 The vaporization device 30 Fig. 2 comprises vaporizer 40 which
11 includes a pillar 60 extending upwardly into the device. Holder 42, to
12 the extent there is one in the device of Fig. 2, is defined by a bottom
13 portion of pillar 60. The device 30 of Fig. 2 further includes a
14 thermally conductive material 50 defining a void 52 therein. Material 50
15 is shaped to define an outer periphery 54 comprising sides 56 and
16 ends 58. Material 50 is further configured to form pillar 60, which
17 protrudes upwardly from one of the ends 58 and into a region between
18 sides 56. The outlet region 36 and inlet region 34 of the device of
19 Fig. 2 extend through material 50 to define gas passageways into and out
20 of void region 52.

21 Non-vapor-state-material inlet 32 comprises three separate capillaries
22 (32a, 32b, and 32c) extending through an end 58 and terminating above
23

1 pillar region 60. Non-vapor-state material 33 comprises three separate
2 materials (33a, 33b and 33c), which can comprise, for example, liquids.

3 In operation, material 50 is heated and non-vapor state materials
4 33a, 33b and 33c are flowed through inlets 32a, 32b and 32c and onto
5 pillar region 60. The non-vapor state materials are then vaporized upon
6 contact with a heated vaporization surface of pillar region 60 to form
7 a vapor 20. Such vapor 20 then flows to outlet 36 and out of
8 device 30. The three materials 33a, 33b and 33c can comprise, for
9 example, $\text{Ba}(\text{THD})_2$, $\text{Sr}(\text{THD})_2$, and $\text{Ti}(\text{O-iPr})_2(\text{THD})_2$, in, for example,
10 applications wherein a vapor is to be formed for deposition of BST. In
11 the above formulas, THD stands for bis(2,2,6,6-tetramethyl-3,5-
12 heptanedionate) ($\text{C}_{11}\text{H}_{19}\text{O}_2$), and O-iPr stands for isopropoxide ($\text{C}_3\text{H}_7\text{O}$).

13 In the above-described application for forming BST, material 50
14 and pillar region 60 are preferably heated to a temperature of
15 about 250°C ($\text{Ba}(\text{THD})_2$ vaporizes at about 212°C). Also, the carrier
16 gas 35 preferably comprises a temperature of about 250°C. Carrier
17 gas 35 can comprise, for example, nitrogen or helium.

18 A second prior art vaporization device 30 is described with
19 reference to Fig. 3. In the device of Fig. 3, vaporizer 40 comprises a
20 heated frit, and holder 42 comprises a pair of projections extending from
21 sides of frit 40. The embodiment of Fig. 3 further comprises an outer
22 periphery 70 surrounding frit 40 and defining a void 72 therein. Inlet
23 region 32 comprises three separate capillaries (labeled as 32a, 32b

1 and 32c) which extend through periphery 70 and into void regions 72.
2 Capillaries 32a, 32b and 32c are configured such that non-vapor-state-
3 materials 33a, 33b and 33c flow through capillaries 32a, 32b and 32c and
4 onto a vaporization surface 44 of frit 40.

5 In operation, frit 40 is heated to a temperature such that
6 materials 33a, 33b and 33c are vaporized upon contact with surface 44
7 to form a vapor 20 which exits device 30 through outlet port 36. Also,
8 a carrier gas 35 is injected into device 30 through inlet port 34 to flow
9 vapor 20 out of device 30. Materials 33a, 33b and 33c can comprise,
10 for example, $\text{Ba}(\text{THD})_2$, $\text{Sr}(\text{THD})_2$, and $\text{Ti}(\text{O-iPr})_2(\text{THD})_2$, for formation
11 of BST. In such embodiments, frit 40 is preferably heated to a
12 temperature of about 250°C, and carrier gas 35 is also preferably heated
13 to a temperature of about 250°C. The system described with reference
14 to Fig. 3 is a diagrammatic, schematic view of an Advanced Delivery and
15 Chemical Systems vaporizer. (Advanced Delivery and Chemical Systems
16 (ADCS), 7 Commerce Drive, Danbury Ct. 06810-4169.)

17 A problem with the prior art devices described above is that
18 materials injected into the devices can decompose to form deposits on
19 vaporization surfaces 44. A reason that the deposits form can be, for
20 example, that the vaporization temperature is close to a decomposition
21 temperature for non-vapor-state-materials 33 injected into devices 30.
22 The deposits can decrease the effectiveness of vaporization surfaces 44,
23 and can, for example, cause clogging and other problems due to

1 particulate formation. Accordingly, it would be desirable to develop
2 methods for cleaning deposits from surfaces 44.

3 4 SUMMARY OF THE INVENTION

5 In one aspect, the invention encompasses a method of utilizing a
6 vaporization surface as an electrode to form a plasma within a vapor
7 forming device.

8 In another aspect, the invention encompasses a method of chemical
9 vapor deposition. A vaporization surface is provided and heated. At
10 least one material is flowed past the heated surface to vaporize the
11 material. A deposit forms on the vaporization surface during the
12 vaporization. The vaporization surface is then utilized as an electrode
13 to form a plasma, and at least a portion of the deposit is removed with
14 the plasma.

15 In another aspect, the invention encompasses a vapor forming
16 device. Such device includes a non-vapor-state-material input region, a
17 vaporization surface, and a flow path between the non-vapor-state-material
18 input region and the vaporization surface. The device further includes
19 a vapor-state-material output region, and a vapor flow path from the
20 vaporization surface to the vapor-state-material output region.
21 Additionally, the device includes a first plasma electrode spaced from the
22 vaporization surface, and plasma generation circuitry configured to utilize
23

1 the vaporization surface as a second plasma electrode such that a plasma
2 can be formed between the first and second plasma electrodes.

3 4 **BRIEF DESCRIPTION OF THE DRAWINGS**

5 Preferred embodiments of the invention are described below with
6 reference to the following accompanying drawings.

7 Fig. 1 is a diagrammatic view of a prior art chemical vapor
8 deposition apparatus.

9 Fig. 2 is a diagrammatic view of a prior art vaporization device.

10 Fig. 3 is a diagrammatic view of a second prior art vaporization
11 device.

12 Fig. 4 is a diagrammatic view of a vaporization device encompassed
13 by the present invention.

14 15 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

16 This disclosure of the invention is submitted in furtherance of the
17 constitutional purposes of the U.S. Patent Laws "to promote the progress
18 of science and useful arts" (Article 1, Section 8).

19 In a particular aspect, the invention encompasses modification of
20 a vaporization device 30 (exemplary vaporization devices are described
21 above with reference to Figs. 1-3) to enable plasma cleaning of
22 vaporization surface 44. Such aspect is described with reference to
23 Fig. 4. In referring to Fig. 4, similar numbers will be utilized as were

1 used above in describing the prior art devices of Figs. 1-3, with the
2 suffix "d" utilized to indicate features of the structure of Fig. 4.

3 Fig. 4 illustrates a vaporization device 30d comprising a
4 vaporization material 40d having a vaporization surface 44d.
5 Material 40d preferably comprises an electrically conductive material, such
6 as, for example, stainless steel.

7 In the exemplary shown embodiment, vaporization material 40 is
8 supported by a holder 42d. It is to be understood, however, that
9 holder 42d is optional. Device 30d further comprises a non-vapor-state-
10 material inlet 32d, and a source 46d of non-vapor-state material 33d.
11 Additionally, device 30d comprises a carrier gas inlet 34d into which a
12 carrier gas 35d is flowed, and a vapor-state-material outlet 36d from
13 which vapor-state material 20d exits device 30d.

14 Device 30d can comprise, for example, the components described
15 above with reference to Figs. 1-3 for vaporizing a non-vapor-state-
16 material. However, in contrast to the prior art vaporization apparatuses
17 described above with reference to Figs. 1-3, the device 30d of Fig. 4
18 comprises an electrode 100 and circuitry 102 extending between electrode
19 100 and vaporization material 40d. Electrode 100 and circuitry 102 are
20 configured to generate a plasma 110 between electrode 100 and
21 material 40d. Accordingly, device 30d is configured to utilize
22 vaporization material 40d as an electrode for generating a plasma 110.
23

1 Plasma 110 can be utilized to clean deposits from vaporization
2 surface 44d. In the shown embodiment, circuitry 102 comprises a power
3 source 103 which provides RF energy to electrode 100. Power
4 source 103 can also be utilized to provide a bias to vaporization
5 material 40d. Alternatively, power can be provided to material 40d, and
6 a bias provided to electrode 100. In yet other alternative embodiments,
7 power can be provided to one of electrode 100 or material 40d, and the
8 other of electrode 100 and material 40d can be maintained at ground
9 potential.

10 In an exemplary application, plasma 110 is formed by providing an
11 energy of from about 200 watts to about 2,000 watts to one of either
12 electrode 100 or material 40d, with a preferred energy being
13 about 500 watts. A temperature within device 30d is maintained at
14 about 250°C during formation of plasma 110, and a pressure is
15 maintained at less than or equal to about 1 Torr, and greater
16 than 0 Torr.

17 Plasma 110 can be formed from gases comprising one or more of
18 Cl₂, CCl₄, CF₄, CHF₃, O₂, SF₆, NF₃, CCl₃F, CClF₃, C₂F₆, H₂, C₃F₈, and
19 O₃. Such gases can be injected through carrier gas inlet port 34d, or
20 through a separate port (not shown) provided within device 30d. In an
21 exemplary application, a plasma gas comprising one or more of Cl₂, CCl₄
22 and CF₄ is flowed into device 30d at a rate of from about 1 standard
23 cubic centimeter per minute (sccm) to about 2000 sccm. Also, in the

1 exemplary application, electrode 100 is provided with an RF power of
2 from about 200 watts to about 2,000 watts, and material 40d is provided
3 with a bias of from about -1,000 volts to about -20,000 volts. The
4 negative bias produces a positive/negative attraction such that plasma ions
5 are drawn rapidly to vaporization surface 44d for cleaning of the surface.

6 Device 30d can be incorporated into a prior art chemical vapor
7 deposition apparatus, such as, for example, the apparatus 10 described
8 with reference to Fig. 1. In such application, device 30d is in gaseous
9 communication with chemical vapor deposition reactor 12 such that vapor
10 20d flows from outlet 36d into vapor deposition reactor 12. Such vapor
11 can then be utilized to deposit a material over substrate 16. At periodic
12 intervals, a flow of non-vapor-material into device 30d is stopped, and
13 plasma 110 is formed within device 30d to clean vaporization
14 surface 44d. The flow of non-vapor-material 33d into device 30d can be
15 stopped by providing a valve (not shown) between source 46d and
16 inlet 32d.

17 Although the invention is described above with reference to a
18 vaporization device incorporated as part of a chemical vapor deposition
19 apparatus, it is to be understood, that the invention can be utilized in
20 other applications wherein vapor is generated. Such other applications
21 can include, for example, deposition of thin films for wear resistance or
22 corrosion resistance.
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1 In compliance with the statute, the invention has been described
2 in language more or less specific as to structural and methodical
3 features. It is to be understood, however, that the invention is not
4 limited to the specific features shown and described, since the means
5 herein disclosed comprise preferred forms of putting the invention into
6 effect. The invention is, therefore, claimed in any of its forms or
7 modifications within the proper scope of the appended claims
8 appropriately interpreted in accordance with the doctrine of equivalents.

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